

## TREATMENT OF NO<sub>x</sub> SORBER REGENERATION GAS

5 This invention relates to treatment of NO<sub>x</sub> in engine exhaust gas, more particularly to the treatment of NO<sub>x</sub> sorber regeneration gas in the exhaust of a lean-burn reciprocating engine.

10 It has been proposed to remove such NO<sub>x</sub> by sorption in a basic oxidic material, then regenerating that material and concurrently converting NO<sub>x</sub> to N<sub>2</sub> with an agent, which is a reductant or a NO<sub>x</sub>-specific reactant. This process is subject to the problem of how to limit or avoid emission to atmosphere of such agent, which is commonly used in excess and thus is not 100% reacted.

15 In the ensuing description and claims: terms based on the word 'sorb' will be used to denote 'absorb' or 'adsorb' or any occurrence of both such processes; and metal compounds effective to sorb NO<sub>x</sub> will be referred as 'oxides', with the understanding that this term includes other oxidic compounds such as hydroxides and carbonates effective as NO<sub>x</sub> sorbents and present in the conditions of exhaust gas  
20 treatment.

EP-B-0341832 (incorporated herein by reference) describes a process for combusting particulate matter in diesel exhaust gas, which method comprising oxidising nitrogen monoxide in the exhaust gas to nitrogen dioxide on a catalyst,  
25 filtering the particulate matter from the exhaust gas and combusting the filtered particulate matter in the nitrogen dioxide at up to 400°C. Such a system is available from Johnson Matthey and is marketed as the CRT®.

A problem associated with NO<sub>x</sub> sorber regeneration is that it generates a pulse  
30 of enriched exhaust gas containing unburned hydrocarbon (HC) fuel as reductant and NO<sub>x</sub>. Unreacted HC and NO<sub>x</sub> are emitted from the tailpipe and can often be seen as a puff of smoke. Since typical NO<sub>x</sub> sorber regeneration strategies comprise regenerating for a second or so every few minutes, such emissions can contribute to failure of future emission standards for particulates, HC and NO<sub>x</sub>.

We have now developed a technique for treating such NO<sub>x</sub> sorber regeneration gas which reduces this prior art problem.

According to a first aspect, the invention provides a method of treating an  
5 exhaust gas of a lean-burn reciprocating engine containing NO<sub>x</sub>, which method comprising sorbing said NO<sub>x</sub> on at least one NO<sub>x</sub> sorber when the exhaust gas is lean, intermittently contacting the at least one NO<sub>x</sub> sorber with an agent effective to convert NO<sub>x</sub> to N<sub>2</sub> thereby to regenerate the at least one NO<sub>x</sub> sorber and feeding effluent of said intermittent contacting step to the engine inlet.

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According to a second aspect, there is provided a lean-burn reciprocating engine emitting exhaust gas containing NO<sub>x</sub> and having a treatment system comprising at least one NO<sub>x</sub> sorber for sorbing NO<sub>x</sub> when the exhaust gas is lean means for intermittently contacting the at least one NO<sub>x</sub> sorber with an agent effective to convert  
15 NO<sub>x</sub> to N<sub>2</sub> thereby to regenerate the at least one NO<sub>x</sub> sorber and means for feeding effluent of said contacting to the engine inlet.

20 The engine is preferably one equipped for exhaust gas recirculation (EGR) in normal or occasional modes of operation. Alternatively an EGR system can be added to an engine not normally using EGR.

Since feeding the effluent to the engine inlet is merely to dispose of the agent contained in it, its rate of flow is in principle not related to in-engine combustion requirements of conventional EGR. To permit complete recirculation of the effluent without excessive EGR, the system preferably includes at least two NO<sub>x</sub> sorbers arranged in parallel and means for selectively contacting fewer than all of them with the agent. The flow rate of the gas in the NO<sub>x</sub> sorber(s) under regeneration is preferably limited further, to be less than in the remaining NO<sub>x</sub> sorber(s) and  
25 especially to be below the rate of recirculation in an existing EGR system. Such system preferably includes an EGR pump, which determines the flow rate of the recycled effluent.

The agent is conveniently provided by injection into the gas about to enter the NO<sub>x</sub> sorber to be contacted therewith. Reductant may be provided, in a multi-cylinder engine, by intermittently operating fewer than all, preferably one of, the cylinders at a rich or approximately neutral air-fuel ratio, i.e. lambda = 1, and feeding the resulting  
5 exhaust to the NO<sub>x</sub> sorber(s) to be regenerated.

The agent may be a non-selective reductant such as hydrocarbon, CO or hydrogen, injected as such or as compound(s), for example engine fuel, convertible thereto in regeneration conditions over the NO<sub>x</sub> sorber or in a pre-injection step. In an  
10 engine having a common-rail fuel injection system there may be a branch to NO<sub>x</sub> sorber injectors. Non-selective reductant is evidently used if provided by rich/neutral operation of a cylinder.

Alternatively the agent may be a NO<sub>x</sub>-specific reactant, for example a nitrogen  
15 hydride such as ammonia or hydrazine, conveniently provided as a precursor such as an amide for example urea or ammonium carbamate, and possibly fed via a catalyst effective to generate the free hydride.

In addition to the NO<sub>x</sub> removal step the engine exhaust system may include:  
20 upstream of the NO<sub>x</sub> sorber(s), catalytic oxidation of HC and CO to steam and CO<sub>2</sub> and/or of NO to NO<sub>2</sub>; and PM collection preferably downstream of that catalytic oxidation; and/or downstream of the NO<sub>x</sub> sorber(s): catalytic oxidation of residual HC and CO; collection of PM passing the NO<sub>x</sub> sorbers or passing an upstream filter as a result of too small particle size or release by filter flow reversal.  
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When the system includes PM collection, the engine may be designed and calibrated to emit raw exhaust gas containing enough NO<sub>x</sub> for the combustion, after oxidation of NO to NO<sub>2</sub>, of the whole carbonaceous fraction of said PM. Alternatively it may be designed and calibrated to emit, at least temporarily, raw exhaust gas  
30 containing too little NO<sub>x</sub> to complete said combustion, after oxidation of NO to NO<sub>2</sub>. The PM collection means preferably comprises a catalyst effective to promote said combustion and possibly also an oxygen storage material. In each combustion procedure the temperature is at or above the 'balance temperature' for NO<sub>2</sub> or,

additionally, for oxygen, continuously or at intervals when PM has accumulated to a design level. If PM collection uses a filter, provision may be made for intermittent reversal of flow direction therethrough. The engine control system may provide for operation at an inlet air fuel ratio strongly lean for normal running (e.g. a/f = 30) but 5 moderately lean when the temperature is increased for combustion of PM by oxygen (e.g. a/f = 16).

The NO<sub>x</sub> sorbent is typically selected from:

(a) oxides of alkali-, alkaline earth-, rare earth- and transition-, metals capable 10 of forming nitroxy salts of adequate stability in sorbing conditions and of releasing /reacting nitrogen oxides in regenerating conditions.

(b) adsorptive materials such as zeolites, carbons and high-area oxides.

Whichever compounds are used, there is preferably present one or more catalytic materials such as precious metals, especially Pt+Rh, effective to promote reaction of 15 NO<sub>x</sub> with reductant or NO<sub>x</sub>-specific reactant.

The sorbent(s) and catalyst(s) are suitably disposed on a flowthrough monolithic substrates composed of ceramic, wound corrugated metal, or metal foam or sinter or ordered or random-packed wire or flat wire. Filters, if used, may use 20 substrates similar to those of sorbents and catalysts, but in 'filter-grade' permeable to gas and having limited permeability to PM.

To switch gas flow successively from NO<sub>x</sub> sorber(s) in use and under regeneration and/or to reverse the flow direction in a PM filter, the system suitably 25 includes a 4-way valve. Such a valve typically comprises: an outer cylindrical or frusto-conical casing formed with angularly spaced apertures each leading to external flow connections; and deflector means effective to: direct either of two incoming streams to a single outlet; or to direct a single incoming stream to either of two outlets; or to combine two incoming streams into a single stream.

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The valve means comprises also actuator means operating through a seal. The deflector is preferably operable over an arcuate path between two extreme positions at which selected gas flow is required. The deflector may be a 'butterfly'. The valve

casing may be formed with a wall-region of greater diameter corresponding to an intended traverse of the butterfly, and the change to the lesser diameter at the extremities of the traverse is formed as a step conformed to the profile of the butterfly and effective as a seal against gas leakage. The traverse of the butterfly is typically 10  
5 to 20% of the circumference of the casing. If the intermediate non-selective gas flow is required, this is provided by the actuator means.

The deflector means may be provided by a barrel fitting fluid-tightly within the casing and rotatable on an axis transverse to the main direction of fluid flow; formed  
10 along each of two or more radial planes of the barrel at least one fluid tight dividing member; and formed in each division at least one passage open at mutually angled positions about the circumference of the barrel, said positions corresponding to the apertures.

15 The barrel (if used) can be provided by uniting sheet material to define its outer shape and internal passages or by shaping solid material and forming the passages by boring thereinto, so that the residues between bores constitute the dividing members. Each passage normally has an outlet angled to its inlet, for example perpendicularly in a 4-way valve with one inlet connection and two or three outlet connections. In a 4-  
20 way valve having two inlet connections and two outlet connections, each passage may have one inlet and two outlets.

The invention is illustrated by the accompanying drawings, in which:

25 Figure 1 is a flow sheet showing an exhaust gas treatment system in which the valve is used to provide switching flow between two NO<sub>x</sub> sorbers;

Figure 2 is a flow sheet showing an exhaust gas treatment system in which also the valve in a variant is used to provide flow-reversal through a PM filter;

30 Figures 3A, 3B and 3C show enlarged plan views of a valve as used in Figures 1 and 2; and

Figures 4A and 4B show enlarged plan views of a valve as used in Figures 1 and 2.

Referring to Fig 1, in diesel engine 10 the inlet system comprises fuel feed 12, 5 air feed 14 and exhaust gas recirculation (EGR) feed 16, and exhaust gas passes out through manifold 18 to exhaust gas aftertreatment system 19 comprising reactor 20 containing oxidation catalyst 22 consisting of a ceramic honeycomb carrying a washcoat and Pt, followed by PM filter 24. Filter 24 consists of a filter-grade ceramic honeycomb the passages of which are alternately open and closed at the inlet end 10 and, corresponding to the inlet open passages, alternately closed at the outlet end. It may carry a catalyst for soot oxidation, for example Pt or La/Cs/V<sub>2</sub>O<sub>5</sub>. The downstream end of reactor 20 is provided with outlets 26 leading respectively to NO<sub>x</sub> sorbers 30A and 30B, each of which holds a ceramic honeycomb unit carrying an alumina washcoat containing metallic Pt+Rh and barium oxide. Sorbers 30A,B may be 15 provided in separate cans as shown or, to save space, may be in fluid-tight subdivisions of a single can. Each sorber 30A,B is equipped with an injector 32A,B for hydrocarbon from the common-rail system of the engine (connection not shown), or of ammonia or precursor thereof.

20 Each outlet end of sorbers 30A,B is connected to one of the two inlets of 4-way valve 28, whose outlets 34 to the EGR inlet 16 (via a pump, not shown) and 36 to atmosphere align with one or other of the outlets indicated by arrows. Valve 28 is operable between three positions 28X, 28Y and 28Z (Y and Z insets).

25 [NOTE: the two divisions of the valve are referred to as 'LHS' i.e. left hand side and 'RHS' i.e. right hand side, but this is for convenience in understanding the drawings and is not intended to indicate practical construction]

30 In position X both sorbers and both outlets are open: consequently there is no blocked midpoint.

In position Y gas leaving sorber 30A flows only to 34, at the inlet rating of the EGR pump. At the same time the gas from sorber 30B passes out via 36.

5 In position Z operation is analogous, feeding the effluent of 30B to EGR and 30A out via 36.

In normal operation of the engine the exhaust gas, comprising steam( $H_2O_{(g)}$ ), dinitrogen ( $N_2$ ), oxygen ( $O_2$ ), carbon dioxide ( $CO_2$ ), unburned hydrocarbon fuel (HC), carbon monoxide (CO), nitrogen oxides ( $NO_x$ ) and particulate matter (PM), at e.g. 10  $300^{\circ}C$  contacts catalyst 22 over which NO is oxidised to  $NO_2$  and some of the HC and CO are oxidised to steam and  $CO_2$ . It then enters filter 24 on which most of the PM is collected and combusted by reaction with the  $NO_2$  formed in catalyst 24 and possibly also with  $O_2$ . The PM-free gas then undergoes treatment in one of the three modes: 15 28X: sorbers 30A and 30B each sorb  $NO_x$  from approximately half the total gas flowing; sorber outlet gas passes mainly to atmosphere or further treatment at 36, partly to EGR at 34 at the flow rating of the EGR pump (not shown); 28Y: sorber 30A receives a fraction, corresponding to the EGR pump rating, of the total gas flowing and also HC or ammonia injected at 32A. It undergoes regeneration and its effluent is fed to EGR at 34; sorber 30B sorbs  $NO_x$  from a large fraction of the total gas flowing and 20 also its effluent passes to atmosphere or further treatment at 36; 28Z: sorbers 30B and 30A exchange the duties performed at 28Y. The engine management system (not shown) changes from 28X to 28Y or the reverse when the sorber not about to be regenerated is substantially charged with  $NO_x$  but has enough  $NO_x$  sorption capacity in hand to treat the large fraction of the total gas during the regeneration period.

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Referring to figure 2, items 10-19 are the same as in Figure 1 and are indicated schematically. Reactor 20 now contains only catalyst 22. The PM filter, now numbered 25, is in separate vessel 21. It differs in providing for reversal of the direction of flow through the filter. The outlet of reactor 20 is connected to filter 30 vessel 21 by way of single-inlet reversing valve 23, operable in positions 23A and 23B (inset), to give respectively RH to LH or LH to RH flow through filter 25. Leaving filter 25 in either direction, the gas passes through valve 23A or 23B to a bifurcation into outlets 27, each leading to  $NO_x$  sorber 30A or 30B and downstream 4-way valve

28. Operation of valve 28 is the same as in Figure 1, except that outlet 36 to atmosphere is replaced by connection 37 to vessel 38 holding filter 40, the duty of which is to collect PM released from filter 25. Such PM is typically ash, in which event filter 40 may be disposable, such as a fibre or paper filter. Another duty of filter  
5 40 can be to collect any ultra-fine combustible PM not collected by filter 25.

A characteristic of modern diesel engines is that engine out NO<sub>x</sub> and/or exhaust gas temperature can be too low for passive filter regeneration using NO<sub>2</sub> generated catalytically by oxidation of NO as described in EP-B-0341832. One solution to this  
10 problem is to regenerate the filter actively by increasing the temperature in the exhaust system thereby to combust PM on the filter and maintain the back pressure across the filter within acceptable design tolerances. Such active regeneration techniques are described in EP 0758713 (incorporated herein by reference), for example.

15 An advantage of the system disclosed in Figure 2 to the practical application of the CRT® process is that flow reversal in the filter can be used to clear PM that is not readily combusted in NO<sub>2</sub> over a drive cycle. The uncombusted PM can be collected on a second, disposable filter for removal at suitable intervals. Thus, the arrangement has particular use to the retrofit market, providing a practical and economic alternative  
20 to installing expensive and fuel-costly active regeneration apparatus.

Referring to Figures 3A, 3B and 3C and Figures 4A and 4B, each external connection is numbered as in Figures 1 and 2. The plan views shown in these figures relate to an essentially cylindrical valve casing 50 formed internally with  
25 circumferential regions 52 of greater diameter, defining the range of traverse of rectangular butterfly deflector 54 having pivoted operating shaft 56 extending out of the valve casing via a seal to an actuator (not shown). The extremities of the range of traverse are defined by steps 58 between regions differing in diameter, such steps limiting gas leakage out of its intended path.